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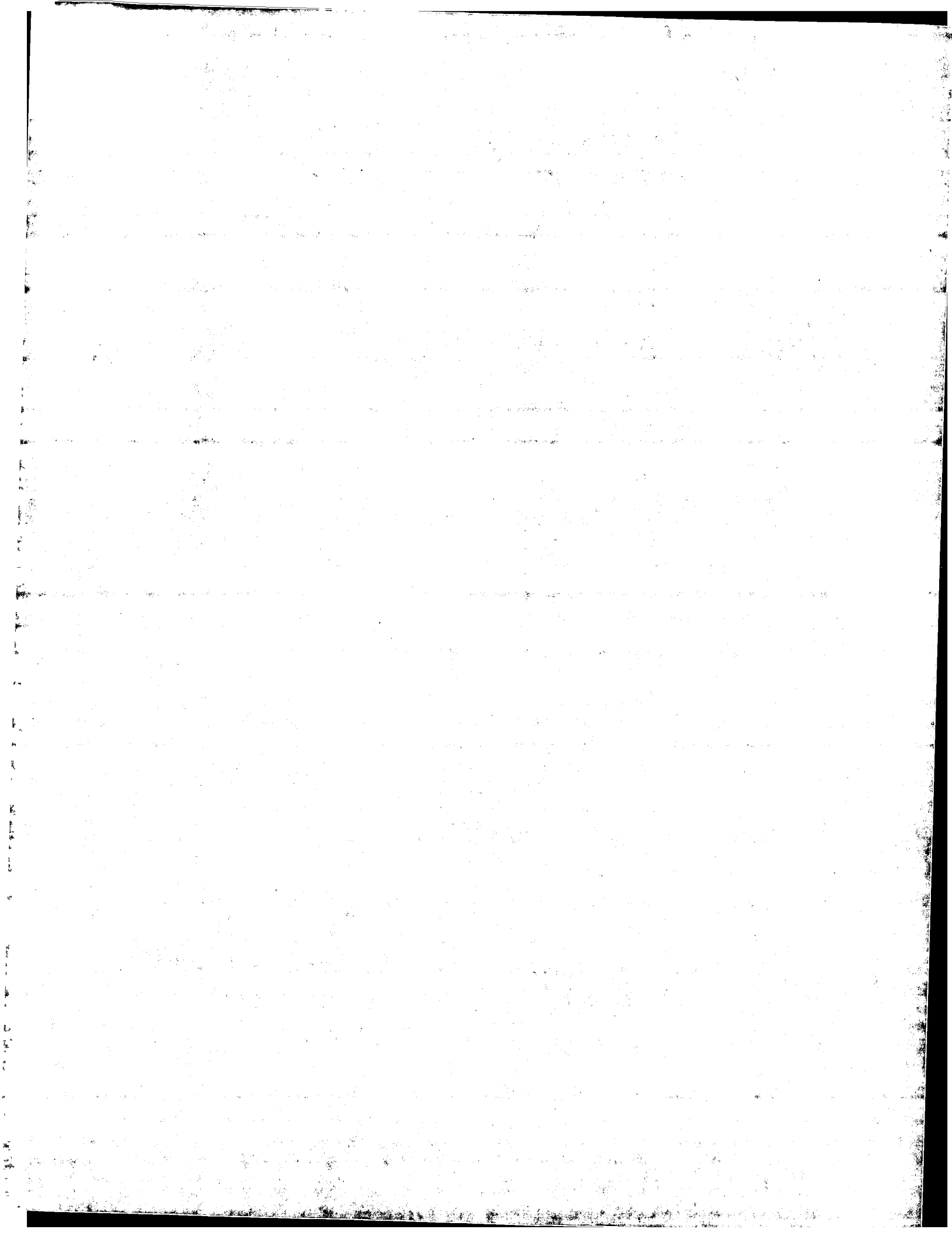
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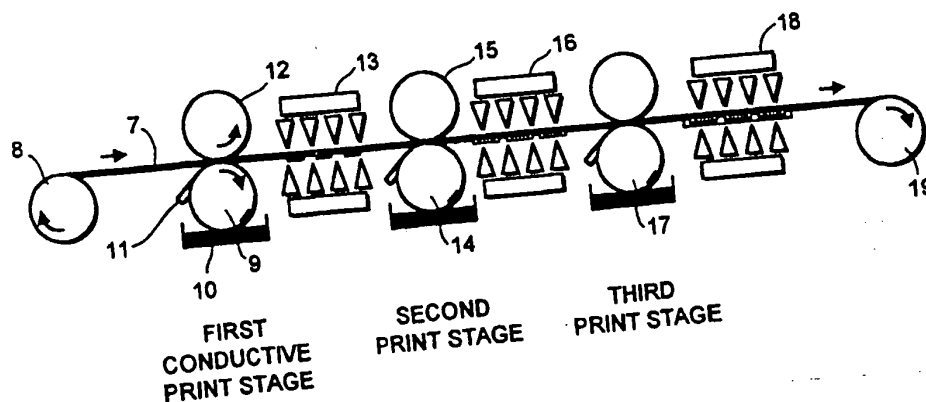
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(57) Abstract

An electrochemical sensor is fabricated by rotogravure printing of electrically conductive ink to form one or more electrodes on a flexible web (7), which may be polymeric. A cylinder (9) coated with a covering defining the shape of the electrodes to be printed may be used. Further cylinders (14, 17) may be used to print further films or layers.

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METHODS OF FABRICATING CHEMICAL SENSORSBackground to the Invention

This invention relates to methods of fabricating chemical sensors, in particular electrochemical sensors incorporating printed electrodes for use in amperometric, potentiometric or voltammetric techniques.

Flat-bed screen printing methods have been the most widely used mass printing technique for the production of electrodes and chemical sensors used in both academic research¹⁻⁶ and industry⁷⁻¹⁰. The process usually entails the application of specialised high viscosity conductive ink formulations which are printed by way of defined screens onto polymer support sheets. Both single or multiple stepwise print-and-dry sequences are often necessary to complete the manufacturing process. By such methods analytical electrodes and chemical sensors for various analytes such as enzyme substrates and heavy metals have been designed^{7,8}. Unfortunately, owing to several production factors, screen print methods for chemical sensor devices seem destined to remain a labour intensive and batch fabrication technology.

EP-A-685735 describes arranging indicator electrodes for a voltammetry device on a flexible tape, wound at one end onto a feed reel and connected at its other end to a take-up reel. Between the reels, the carrier tape runs through a vessel containing liquid to be analysed. The conductive material of the electrodes is applied to the tape by a flat-bed silk screen printing process as described above. For such a tape, screen printing is particularly time-consuming and laborious.

In the printing industry, fast continuous rotogravure machines are well established with fully automated quality controls. Exceptionally high quality standards and

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production capacities, fine line resolution and registration can be achieved by rotogravure printing as seen in journal and packaging manufacture. This highly automated printing technique is continuous and fast (web rates of hundreds of metres/min or greater), relying on finely engraved rotating steel cylinders operating within a web supported reel-to-reel process. Two reels are commonly employed, a pay-off reel supplying the web or material for printing, and a take-up reel at the end of the print process for the collection of printed materials. Cylinders are made by conventional platemaking techniques in addition to electromechanical, electron beam and laser etching methods. The cylinder may be coated with a thin copper or polymer cover, 0.5 to 3 mm into which an engraved structure, i.e. the so called screen and gravure cells, is set.

Such high capacity printers can now apply tens of printed layers (including colours, textures etc) in one reel-to-reel run. Rotogravure presses operate by transferring a printing image present as engraved screens as described, on the printing cylinder to a substrate web which is guided by an accompanying impression cylinder. The engraved regions have a cell structure, diamond as shown in Figure 1, or otherwise, with centre depths ranging from 5 to 30 μm . The important cell and screen variables are the partition width (α) and the square length (l) of the cell. Parameters such as the screen partition ratio which are typically employed are set at 1:3, with a screen ruling of 70 lines/cm. The ink is passed into the cells and then through the action of the impression cylinder the ink is transferred to the printing medium which can be thin organic polymer films, paper or some other web material.

Leppavuori et al¹¹ have described the use of gravure offset printing of silver, platinum and gold inks to form the electrodes of a piezoelectric pressure sensor. However, such flat-bed offset printing is still a batch technique, restricted to solid substrates.

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Summary of the Invention

It is an object of the invention to provide fast, continuous methods of fabricating chemical sensors.

Accordingly, from a first aspect, the present invention
5 comprises a method of fabricating an electrochemical sensor, in which one or more electrodes are formed on a flexible web by rotogravure printing of electrically conductive ink.

In this specification the term "rotogravure" is used to denote any rotary printing process in which ink is applied
10 from an engraved structure, and includes reverse gravure, gravure offset, flexographic, kiss, meter bar, reverse roll, 2 roll nip feed, knife-over-roll, 2 roll pressure, hot melt gravure and size press processes.

Preferably, a series of electrodes is printed, but a
15 continuous conductive layer may also be used to define one or more electrodes. The web may comprise a tape of polymeric material or paper. The web may have a thickness between $10\mu\text{m}$ and $300\mu\text{m}$, preferably between $10\mu\text{m}$ and $15\mu\text{m}$, and may in particular comprise polyethylene terephthalate,
20 polyvinyl chloride, polyamide or cellulose acetate.

The electrically conductive ink preferably contains particles of carbon but may alternatively or additionally contain metallic particles, for example of silver. Preferably, the ink contains an organic polymer binder,
25 such as nitrocellulose, polyamide resin or polystyrene resin, and a solvent such as isophorone or butyl acetate. The viscosity of the ink is preferably less than 100 Pas, i.e. significantly less viscous than conductive screen printing ink.

30 The rotogravure printing preferably takes place using a cylinder coated with a covering of copper or of a polymer, preferably from 0.5 mm to 3 mm in thickness. Preferably the

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covering is engraved with a cellular structure defining the shape of the electrode(s) to be printed. Advantageously, the depth of the engraving is greater than $40\mu\text{m}$ and said depth may be greater than $50\mu\text{m}$. Particularly good results are obtained at a cell depth of $62\mu\text{m}$, in that a continuous conductive film with a low resistance for a given width of electrode is obtained.

Preferably, after printing of the electrode(s), the ink is dried by passing the web through a drier which may comprise an oven or an infra-red or ultra-violet emitter.

In some embodiments of the invention, one or more further films or layers are applied to the sensor by rotogravure printing or coating or lamination, after printing of the electrode(s). The further films or layers may comprise insulating films; analytical reagents such as enzyme reagents; enzyme redox mediators, promoter factors or pH control additives; ion conductive gels which may include water or organic solvents; and/or hydrogels, which may be based on n-vinylpyrrolidones, methacrylate polymers or vinyl-alcohol polymers. Such hydrogel layers can be used to protect, control or enhance the action of the gravure printed sensing layer(s). When gels are printed, enzyme and/or immunochemical reagents may be immobilised within the gel material, along with buffering agents such as citrates, phosphates, hydrogen carbonates or the like to control the pH conditions in the gel phase, preferably to within pH 3-10.

In order to print more than one film, the method preferably comprises the steps of printing the conductive electrode(s) by rotogravure, passing the web through a drier, and then printing one or more further films, passing the web through a further drier after each successive printing operation. It will be appreciated that the web can thus be advanced alternately between respective rotogravure printing and impression cylinders and through driers, in a

fast, continuous process.

From a second aspect, the present invention provides an electrochemical sensor fabricated by the method defined above.

5 From a third aspect, the present invention provides apparatus for fabricating an electrochemical sensor, comprising a covering for a rotogravure printing cylinder, engraved so as to define the shape of electrodes to be
10 printed. Preferably, the covering is of copper or of a polymer and preferably the engraving has a cellular structure. Advantageously, the depth of the engraving is greater than $40\mu\text{m}$, and said depth may be greater than $50\mu\text{m}$ or greater than $60\mu\text{m}$.

From a fourth aspect, the present invention provides an
15 electrically conductive ink for rotogravure printing of electrodes, containing particles of carbon. The ink preferably contains an organic polymer binder, such as nitrocellulose, polyamide resin or polystyrene resin, and preferably a solvent such as isophorone or butyl acetate.
20 The viscosity of the ink is preferably less than 100 Pas, and the conducting particle content is preferably from 20 to 60% by weight.

Brief Description of the Drawings

In order that the present invention may be more readily
25 understood, reference will now be made by way of example only to the accompanying drawings, in which:-

Figure 1 shows a conventional rotogravure cell structure;

Figure 2a shows an electrode which may be printed
30 according to an embodiment of the invention;

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Figure 2b shows a serial arrangement of electrodes as shown in Figure 2a;

Figures 3a, 3b, 4a and 4b are micrographs of conductive films printed according to embodiments of the invention;

5 Figure 5 is a graph showing resistivity of electrodes printed using different formulations of conductive ink;

Figure 6 is a graph showing resistivity of electrodes cured under different conditions;

10 Figure 7 is a schematic perspective view showing use of a chemical sensor fabricated according to one embodiment of the invention;

Figures 8a, 8b and 8c are voltammograms showing alternative uses of the sensor of Figure 7;

15 Figure 9 is a transverse sectional view of an alternative embodiment of sensor; and

Figure 10 is a schematic diagram of apparatus for fabricating sensors according to an embodiment of the invention.

Detailed Description of the Preferred Embodiments

20 Figure 2a shows, with dimensions, one possible configuration of an electrode to be printed according to an embodiment of the invention. As shown in Figure 2b, such electrodes can be printed end-to-end along a narrow tape with a separation of only 0.35 mm between adjacent
25 electrodes. The electrodes can alternatively be printed transversely side by side on the tape.

Figures 3a and 3b show, at greater and lesser magnifications respectively, a film of conductive ink which

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was printed using rotogravure with an engraved cell depth of $41\mu\text{m}$. Although the film appeared continuous to the naked eye, Figure 3b shows that it was discontinuous at the microscopic level.

5 The thicknesses of the conductive films printed according to the invention are smaller, at 2 to $8\mu\text{m}$, than screen printed films. This could result in high cross-track resistance values which are undesirable for many electrochemical sensor applications. For example, using
10 Electrador 5000 screen print carbon ink, (Electra Polymers & Chemical Limited, UK) the dry film cross-track resistance was at least $2\text{ M}\Omega$ due to the poor gravure print characteristics of the ink. Thus, the inks used are specially formulated from commercial screen printing ink
15 formulations by adding solvents such as isophorone and butyl acetate. For example, 33% by total weight of isophorone was added to Electrador 5000, and the resulting dry film had a cross-track resistance of $2\text{ k}\Omega$ or less. When the conductive particle content of the ink was controlled to be within 20
20 to 60% and the ink viscosity to be less than 100 Pa.s , the dry film resistance was $1\text{ k}\Omega$ or less.

The depth of the engraved cell also has a critical effect on the resulting dry-film resistance value. Using solvent modified commercial screen inks, the following
25 results were obtained.

Cell depth	Cross-track resistance
$29\mu\text{m}$	$2\text{ M}\Omega$
$31\mu\text{m}$	$24\text{ k}\Omega$
$33\mu\text{m}$	$2.8\text{ k}\Omega$
$62\mu\text{m}$	$\leq 1\text{ k}\Omega$

30 The reason for the favourable low resistances achieved at extremely large cell depths can be seen from Figures 4a

and 4b which show, at a greater and a lesser magnification respectively, a conductive film printed at a cell depth of $52\mu\text{m}$. The discontinuities observed in Figures 3a and 3b have been eliminated.

5 Figure 5 shows the resistivity of electrodes printed using inks mixed from different proportions of Electrador 5000 and isophorone. Each electrode was cured for 4 hours at 70°C . It can be seen that for proportions of Electrador below 67%, the resistivity was high. Also the viscosity of the ink was too low for effective rotogravure printing. For 10 proportions of Electrador above 90%, not only was the resistivity increased but the ink was viscous and difficult to use. Between 67% and 90% of Electrador, a minimum resistivity of about 2 to 3 $\text{k}\Omega/\text{mm}$ was achieved and the 15 proportion of Electrador selected for subsequent experiments was therefore 75%.

Figure 6 shows the resistivity of electrodes printed using ink mixed with an electric mixer and then cured for different times and at different temperatures. After 5 20 minutes, the resistivity reached a minimum value of about $0.5\text{ k}\Omega/\text{mm}$ for temperatures above 130°C . However, after 10 minutes, the data was less scattered and the resistivity values remained the same. Above 150°C a very small deformation of the polyester support was observed.

25 For lower temperatures such as 90°C , the curing time is more important since after 5 or 10 minutes the solvent is not totally evaporated. It appears that optimum curing occurs at 130°C for 10 minutes.

30 The resistivity values shown in Figure 6 are lower than those shown in Figure 5 due to the use of a fresh sample of Electrador ink and of the electric mixer.

The resistivity of the electrodes can be decreased further by adding silver or gold inks to the carbon ink.

Figure 7 shows an electrochemical sensor comprising a polymeric tape 1 onto which a carbon electrode 2 and a silver/silver chloride reference electrode 3 have been printed. The ink used for printing the reference electrode 3 is similar to that used for the carbon electrode 2, but contains silver particles instead of carbon particles, and also a silver chloride particle addition of, say, 5%, 10% or 15%.

The indicating electrode is more precisely defined by printing an insulating film 4 over the carbon electrode 2, the insulating film having an aperture 5 through which the carbon electrode is accessible. The insulating film 4 is printed using an insulating ink comprising a polymer of vinyl, methacrylate, styrene or cellulose. The insulating ink preferably has a viscosity of less than 1 Pas and the resulting film has a resistance of at least 10 MΩ.

Figure 7 shows the use of the sensor for the electrochemical oxidation of aminophenol. The carbon electrode 2 is suitably polarised with respect to the silver electrode 3 and the current flowing through the carbon electrode is measured to determine the quantity of aminophenol.

The sensor shown in Figure 7 can, of course, be used to detect other analytes. Figures 8a and 8b show the results of a test for presence of ferrocene carboxylic acid in an aqueous electrolyte. Figure 8a is a voltammogram of a control experiment showing the response of the gravure carbon ink film 2 to an aqueous potassium chloride electrolyte (0.1M), over a potential range from -0.4 V to +1 V, versus the silver/silver chloride reference electrode 3. Figure 8b shows the response to the same electrolyte, but containing the ferrocene redox substance, ferrocene carboxylic acid (0.5 mM) and buffered with sodium phosphate (0.2 M).

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Figure 8c is an anodic stripping voltammogram showing the detection of 20 ppb each of lead and cadmium dissolved in 0.15 M nitric acid using the sensor of Figure 7. The measurement time was 20 ms, the measurement pulse 40 ms and the voltage was stepped up from -900 to 200 mV in 6 mV intervals.

In addition to conductive and insulating films, films containing analytical reagents can also be printed. For example, Figure 9 shows a rotogravure glucose sensor comprising a polymer support 1 upon which a carbon indicating electrode 2 and a silver reference electrode 3 have been printed. A further film 6 based on a gel of cellulose polymer, polyvinyl alcohol or polyvinylpyrrolidone and containing glucose oxidase and an electron transfer reagent such as a ferrocene mediator, has been printed on top of the carbon electrode 2. The reagent film 6 effects the oxidation of glucose which can then be detected by the electrode device.

Many other films and layers can also be applied to the sensors of the invention by rotogravure printing. These include ion conductive gels¹² and hydrogel membranes¹³⁻¹⁵; and can contain a wide range of reagents such as metal binding ligands for metal ion analysis.

The support upon which the conductive and other films are printed generally comprises an organic polymer film of thickness between 10 μ m and 300 μ m. Thicknesses at the lower end of this range, for example 12 μ m are preferred, since this facilitates the winding of very long webs or tape onto reels.

Figure 10 shows a continuous reel-to-reel process in which electrodes and two further films are printed sequentially onto a web 7. The web is fed from a pay-off reel 8, onto which it is initially wound, to a first rotogravure printing cylinder 9. The first printing

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cylinder 9 is continuously supplied with conductive carbon ink which is scraped from the covering of the cylinder by a doctor blade 11 so that ink only remains in the engraved structure.

5 The web 7 is sandwiched between the first printing cylinder 9 and a first impression cylinder 12 and conductive electrodes are thus printed onto the web. The web then passes through a first drier, which may be a conventional thermal oven or an infra-red or ultra-violet unit. The
10 gravure printed conductive film can be rapidly dried, since it has a thickness less than 5 μ m.

Subsequently, the web 7 passes between a second printing cylinder 14 and second impression cylinder 15, in order to print an additional film such as a reagent layer.
15 The second layer is dried in a second drier 16. A third printing cylinder 17 is used to print a third film such as an insulating layer, and this is dried in a third drier 18. Finally, the finished web is wound onto a take-up reel 19. The web comprises a very large number of identical
20 electrochemical sensors, and may be used in a continuous sensing method such as that described in EP-A-685735. Alternatively, the individual sensors may be dissected from the web.

It will be appreciated that the invention, as described
25 above, provides a fast and continuous method of fabricating electrochemical sensors.

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CLAIMS

1. A method of fabricating an electrochemical sensor, in which one or more electrodes are formed on a flexible web by rotogravure printing of electrically conductive ink.
- 5 2. A method according to claim 1, wherein a series of electrodes is printed along the web.
3. A method according to claim 1, wherein a continuous conductive layer is printed to form the or each electrode.
- 10 4. A method according to claim 1, 2 or 3 wherein the web comprises a polymeric material.
5. A method according to claim 4, wherein the web comprises polyethylene terephthalate, polyvinyl chloride, polyamide or cellulose acetate.
- 15 6. A method according to any preceding claim, wherein the web has a thickness between $10\mu\text{m}$ and $300\mu\text{m}$.
7. A method according to claim 6, wherein the web has a thickness between $10\mu\text{m}$ and $15\mu\text{m}$.
8. A method according to any preceding claim, wherein
20 the ink contains particles of carbon.
9. A method according to any preceding claim, wherein the ink contains metallic particles.
10. A method according to any preceding claim, wherein the ink contains an organic polymer binder, such as
25 nitrocellulose, polyamide resin or polystyrene resin.
11. A method according to any preceding claim, wherein the ink contains a solvent such as isophorone or butyl

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acetate.

12. A method according to any preceding claim, wherein the rotogravure printing takes place using a cylinder coated with a covering, the covering being engraved with a structure defining the shape of the electrode(s) to be printed.

13. A method according to claim 12, wherein the depth of the engraving is greater than $40\mu\text{m}$.

14. A method according to claim 13, wherein the depth of the engraving is greater than $50\mu\text{m}$.

15. A method according to any preceding claim, comprising a step of drying the ink after printing of the electrode(s) by passing the web through a drier.

16. A method according to claim 15, wherein after the drying step, one or more further films or layers are applied to the sensor by rotogravure printing or coating or lamination.

17. A method according to claim 16, wherein an insulating film is applied.

18. A method according to claim 16 or 17, wherein an analytical reagent film is applied.

19. A method according to claim 16, 17 or 18, wherein an ion conductive gel is applied.

20. A method according to claim 16, 17, 18 or 19, wherein a hydrogel is applied.

21. A method according to any one of claims 16 to 20, comprising the steps of printing the electrode(s), passing the web through the drier, printing further film or layer,

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passing the web through a further drier, and optionally printing still further films or layers and passing the web through further driers.

22. An electrochemical sensor comprising a flexible
5 web having one or more electrodes of conductive ink printed thereon by rotogravure.

23. Apparatus for fabricating an electrochemical sensor, comprising a metallic or polymeric cover for a rotogravure cylinder, engraved with a cellular structure
10 defining the shape of electrodes to be printed.

24. Apparatus according to claim 23, wherein the depth of the engraving is greater than $40\mu\text{m}$.

25. Apparatus according to claim 24, wherein the depth of the engraving is greater than $50\mu\text{m}$.

15 26. Apparatus according to claim 25, wherein the depth of the engraving is greater than $60\mu\text{m}$.

27. An electrically conductive ink for rotogravure printing of electrodes, containing particles of carbon.

28. An ink according to claim 27, containing an
20 organic polymer binder, such as nitrocellulose, polyamide resin or polystyrene resin.

29. An ink according to claim 27 or 28 containing a solvent such as isophorone or butyl acetate.

30. An ink according to claim 27, 28, 29, having a
25 viscosity less than 100 Pas.

31. An ink according to claim 27, 28, 29 or 30, having a conductive particle content between 20% and 60% by weight.

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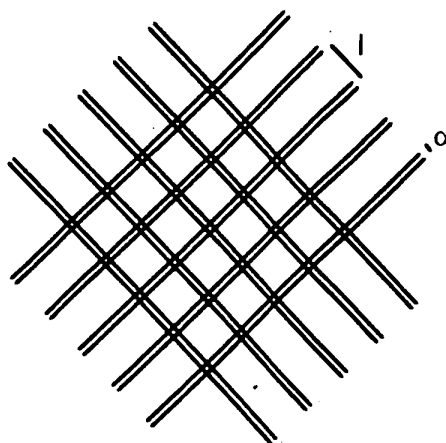


FIG. 1

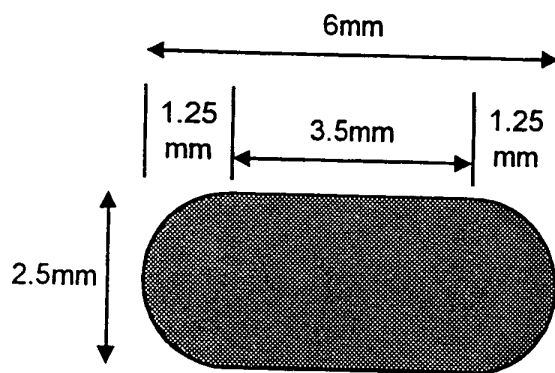


FIG. 2a

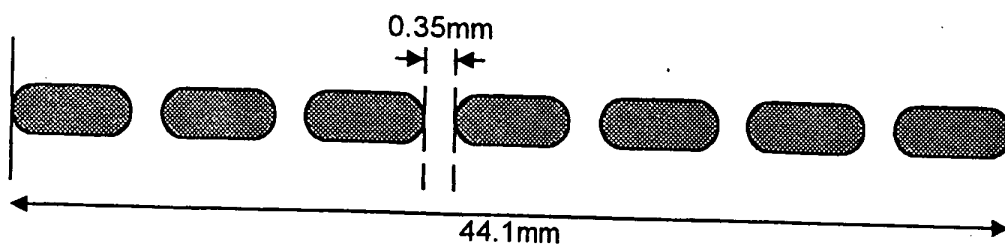


FIG. 2b

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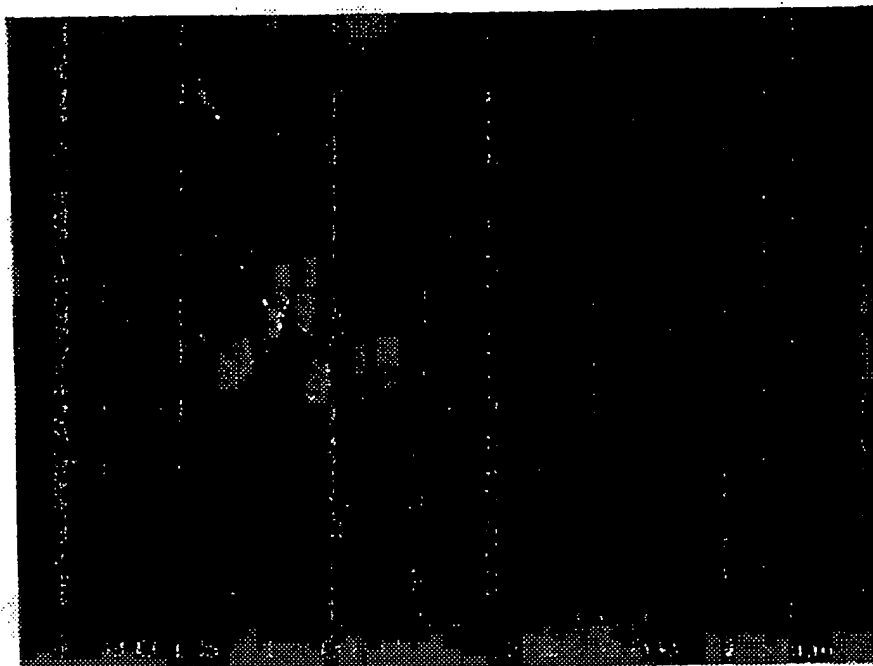
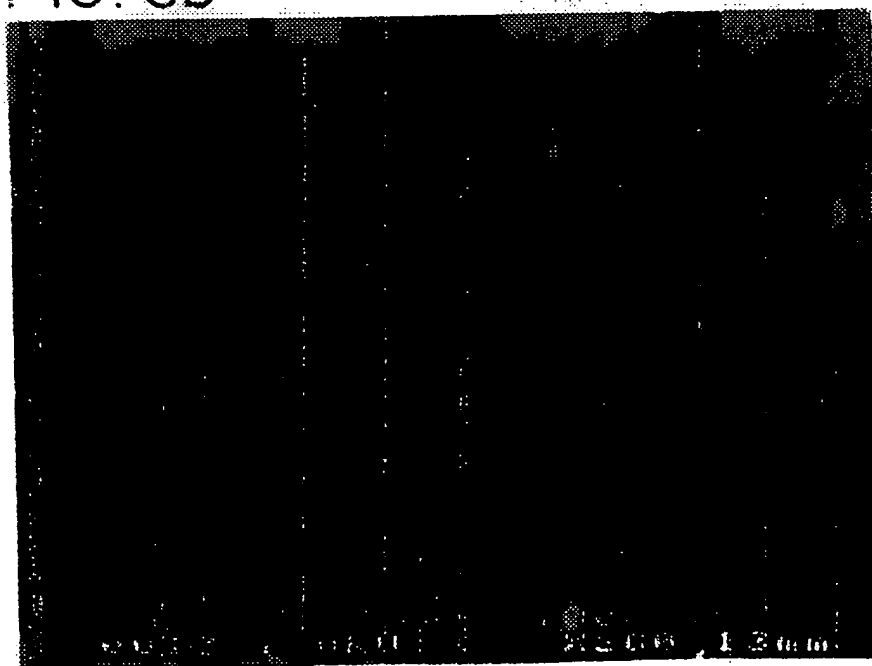


FIG. 3a

41 μ m ROTOGRAVURE PRINT

FIG. 3b



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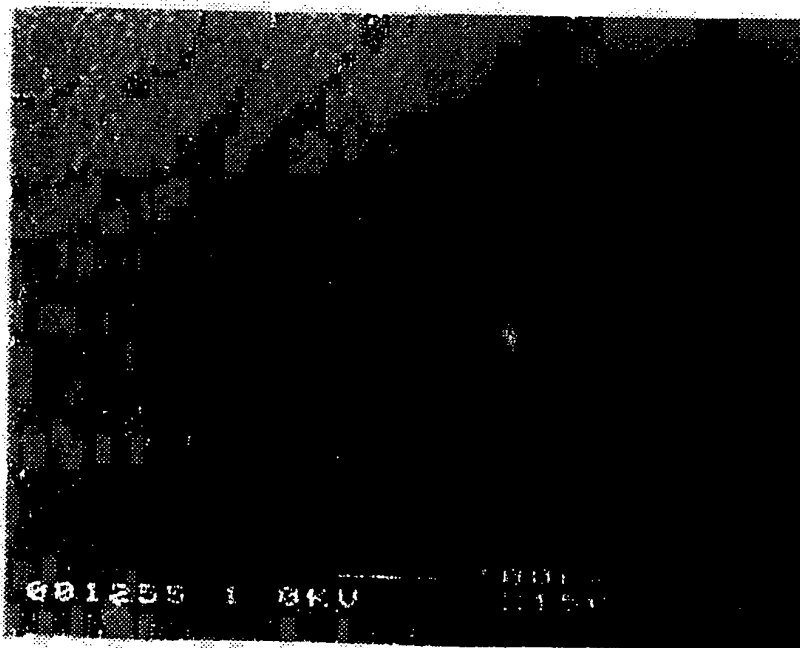
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FIG. 4a

52 µm ROTOGRAVURE PRINT

FIG. 4b



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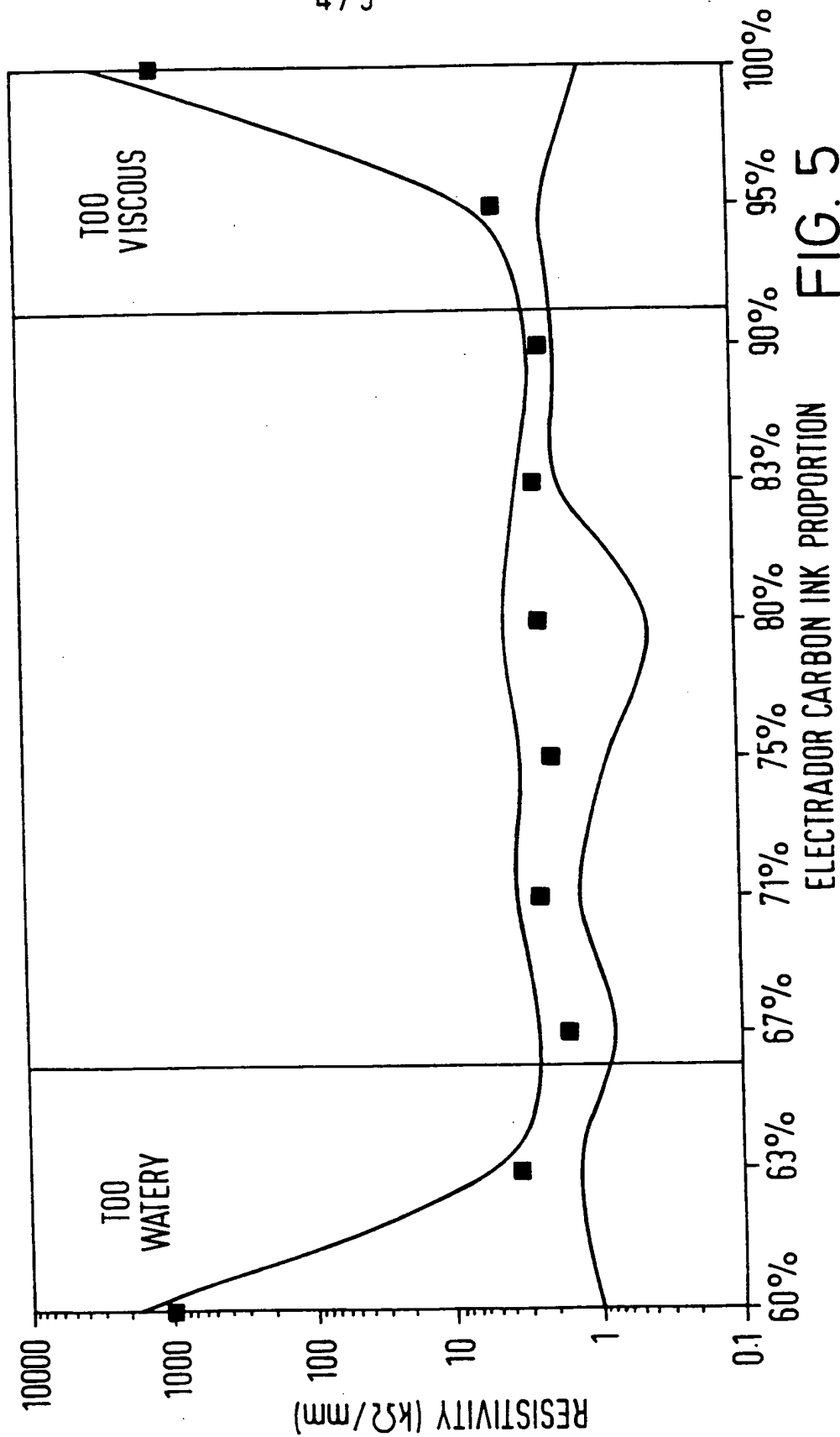
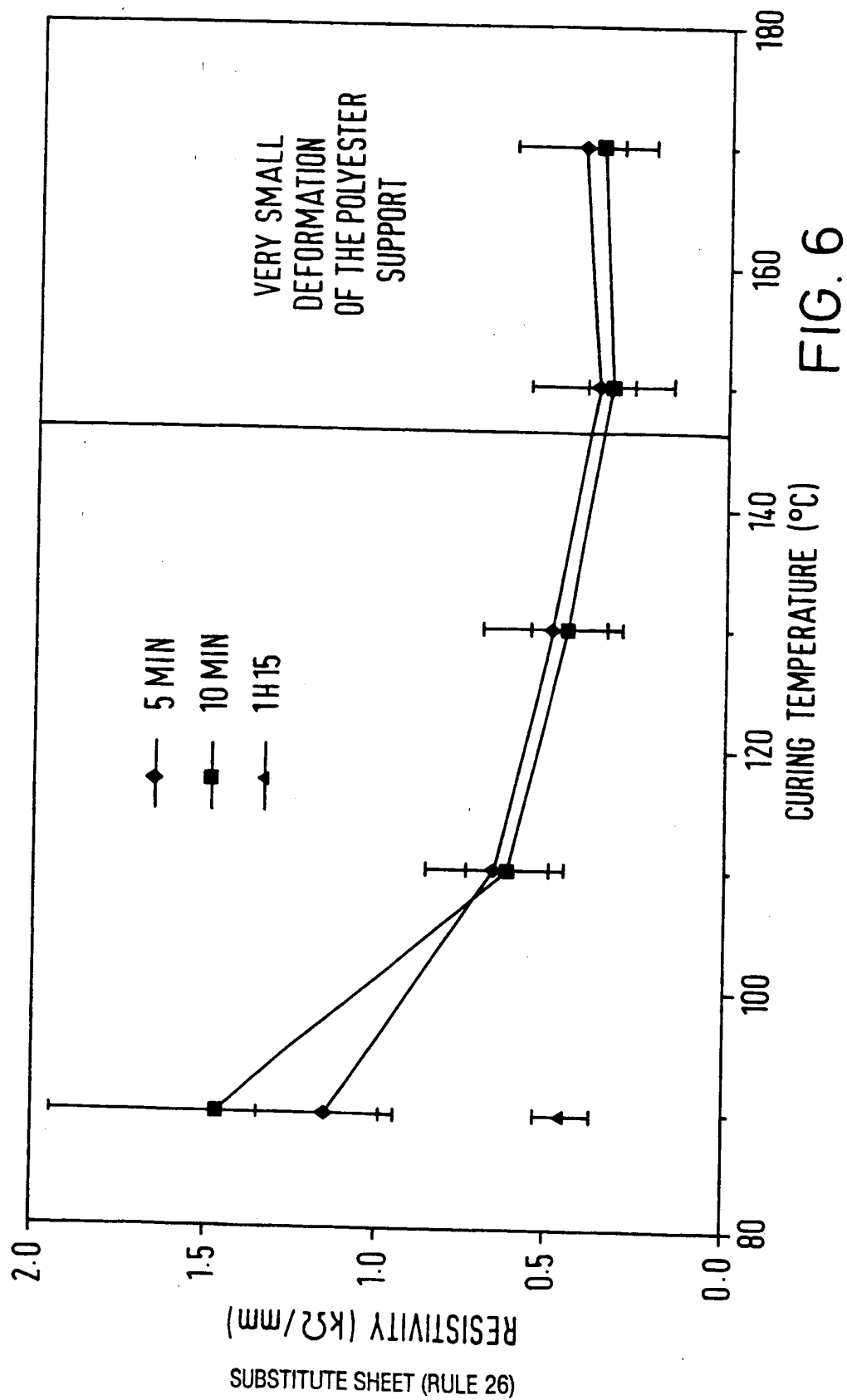


FIG. 5

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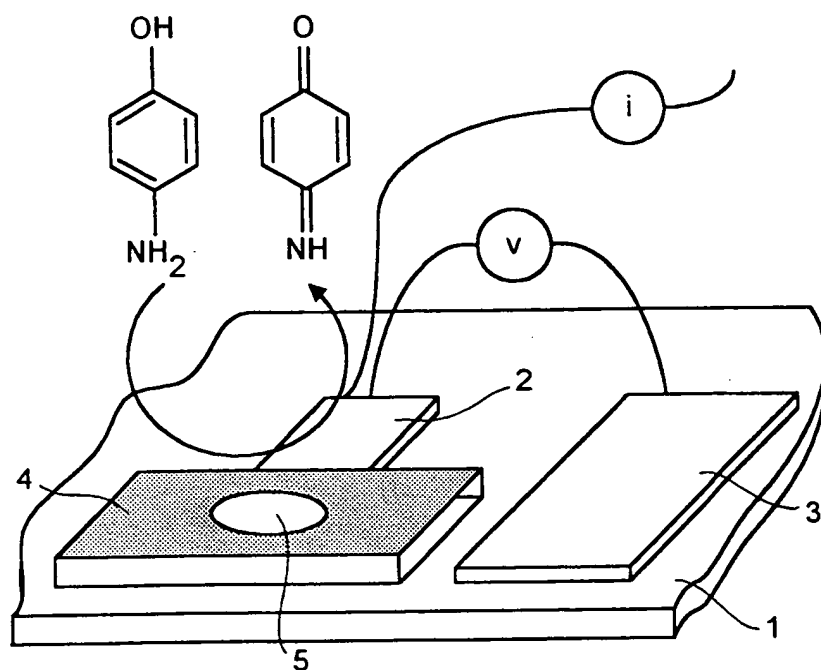


FIG. 7

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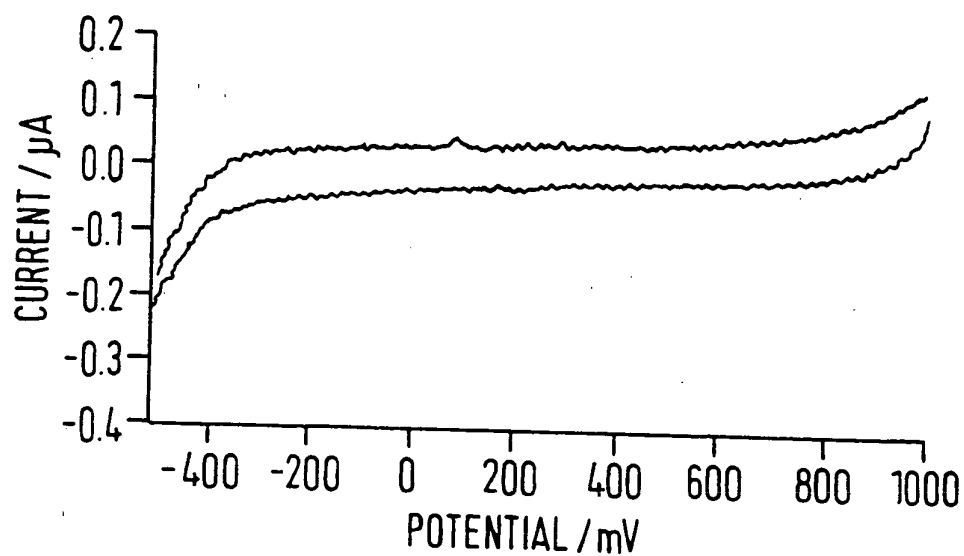


FIG. 8a

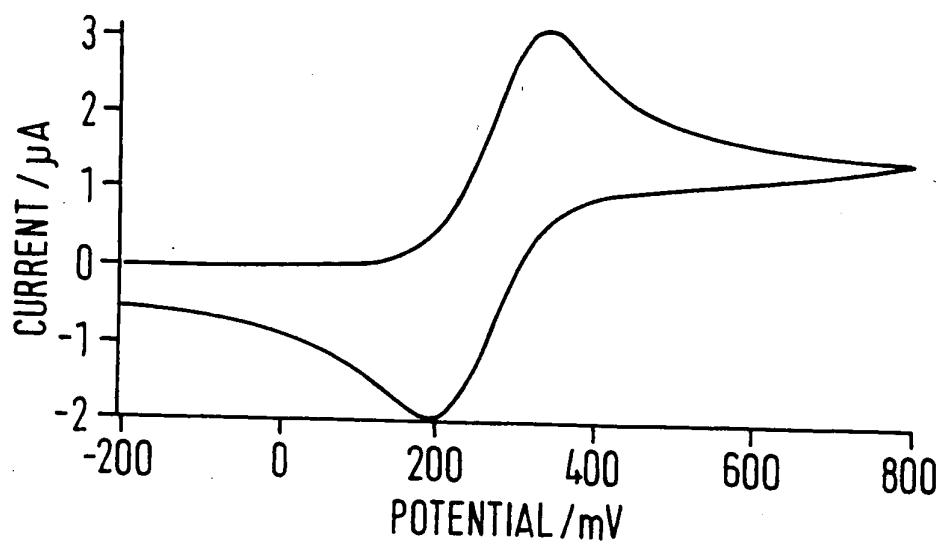


FIG. 8b

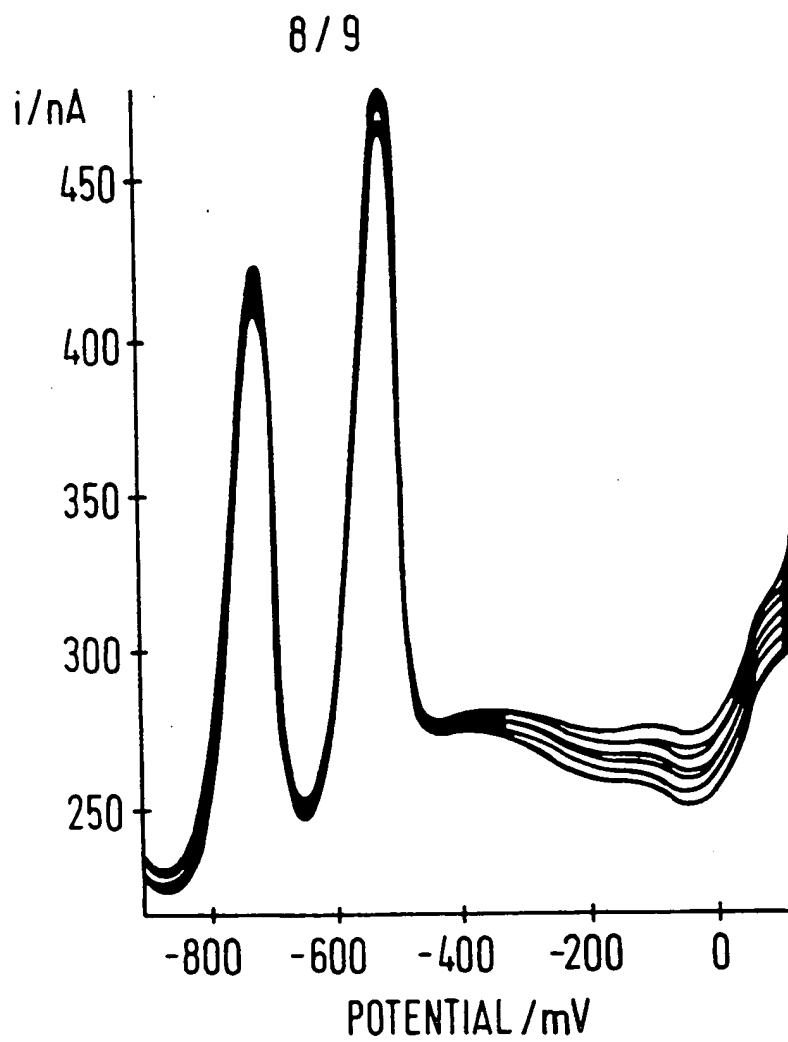
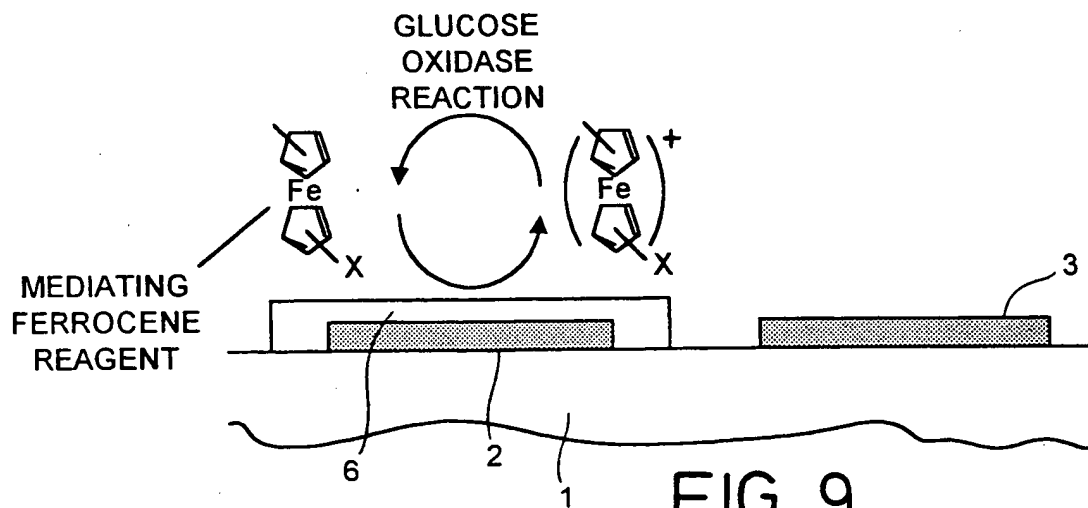


FIG. 8c



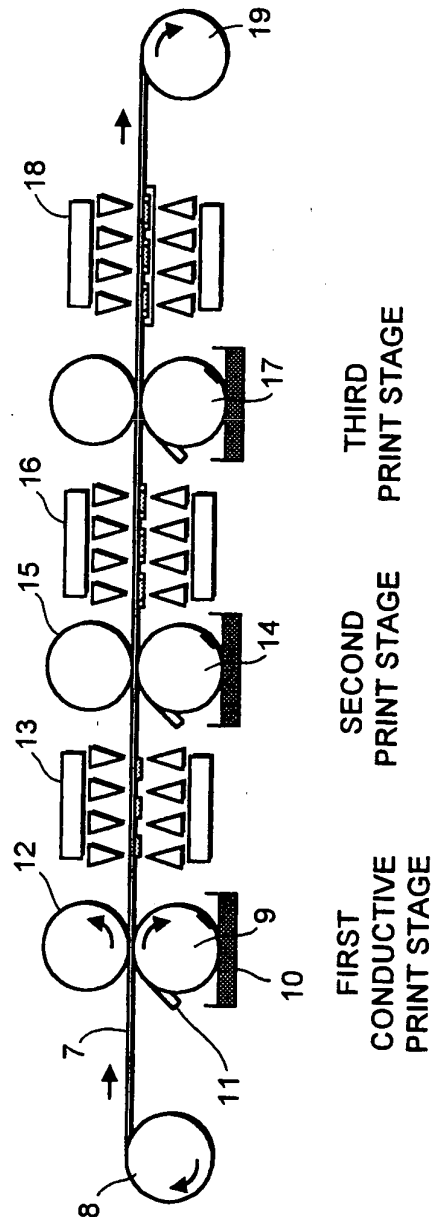


FIG. 10

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/GB 98/00857

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/30

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N B41F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 685 735 A (METROHM AG) 6 December 1995 cited in the application see the whole document ---	1,22,23, 27
A	S. LEPPÄVUORI: "A novel thick-film technique, gravure offset printing, for the realization of fine-line sensor structures" SENSORS AND ACTUATORS, A, vol. 41-42, 1994, pages 593-596, XP000449988 cited in the application see the whole document ----- -/--	1,22,23, 27

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

9 July 1998

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PCT/GB 98/00857

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 28401 A (ENVIROMED PLC ;BIRCH STEPHEN (GB); BOLBOT JOHN (GB); COSTA ERIC D) 8 December 1994 see page 7, line 5 - line 12 ---	1
A	U. BILITEWSKI: "thick film biosensors for urea" SENSORS AND ACTUATORS, B, vol. B7, 1992, pages 321-326, XP000286981 see page 322, left-hand column, last paragraph ---	1
A	US 2 142 147 A (G. J. PRAGER) 3 January 1939 see figure 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/GB 98/00857

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			CA 2149834 A	04-12-1995
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US 2142147	A	03-01-1939	NONE	

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<p>(21) International Application Number: PCT/GB98/00857</p> <p>(22) International Filing Date: 20 March 1998 (20.03.98)</p> <p>(30) Priority Data: 9705922.4 21 March 1997 (21.03.97) GB</p> <p>(71) Applicant (for all designated States except US): METROHM AG [CH/CH]; CH-9101 Herisau (CH).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): L'HOSTIS, Eva, Helga, Annie [CH/CH]; Avenue de Beaulieu 33, CH-1004 Lausanne (CH). GIRAULT, Hubert, Hugues [FR/CH]; En Verney, CH-1088 Ropraz (CH). OSBORNE, Murray, Douglas [GB/CH]; Avenue du Mont d'Or 55, CH-1007 Lausanne (CH). LAGGER, Gregoire [CH/CH]; Rue des Bains 42, CH-1205 Genève (CH). SCHAEFER, Helwig [DE/CH]; Giebelhalde 5, CH-9100 Herisau (CH). LOYALL, Uwe [DE/CH]; Saumstrasse 15, CH-9100 Herisau (CH).</p> <p>(74) Agent: MANATON, Ross, Timothy; J.Y. & G.W. Johnson, Kingsbourne House, 229-231 High Holborn, London WC1V 7DP (GB).</p>	<p>(81) Designated States: US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>	
<p>(54) Title: METHODS OF FABRICATING CHEMICAL SENSORS</p> <div data-bbox="375 1199 1377 1562"> </div>		
<p>(57) Abstract</p> <p>An electrochemical sensor is fabricated by rotogravure printing of electrically conductive ink to form one or more electrodes on a flexible web (7), which may be polymeric. A cylinder (9) coated with a covering defining the shape of the electrodes to be printed may be used. Further cylinders (14, 17) may be used to print further films or layers.</p>		

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